

A Study On Conceptual Design Of Butyl Acetate Reactive Distillation Column

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Abstract

Reactive distillation (RD) has attracted chemical engineers from almost last five decades due to the advantages offered by it. The present paper reports development of some basic tools required to carry out conceptual design of Reactive Distillation Process with reference to Butyl Acetate system.

Conceptual design tools developed include Reactive VLE data simulation including distillation lines, Residue Curve Maps (RCM) simulation and Reactive Flash simulation.

For all the simulations, algorithms reported in literature are used after suitable modification as well as improvement. **Isobaric** Reactive VLE data simulation is done using modified UNIFAC, NRTL and models for liquid phase non-ideality and association non-ideality in vapor phase. Distillation lines are generated using this simulation.

RCM simulation is performed using equilibrium approach as well as kinetically controlled approach. RCM generation has options for heating policies leading to autonomous as well as non-autonomous ODEs.

Reactive flash simulations are performed for various combinations of composition and temperature to elucidate the effects of feed ratios and operating temperature ranges.

MATLAB[®] has been used for development of all programs used in simulations. Results of simulations for Butyl Acetate system are discussed and analyzed in detail for feasibility

Key Words:

Reactive Distillation, Distillation Lines, RCM, Reactive Flash, Butyl Acetate, MATLAB.

Introduction

In Chemical Engineering major separation energy is utilised in the downstream processing of the reactor effluent. The downstream processing of reactor effluent is quite complex, especially when azeotropes are encountered. A significant simplification of such process is often feasible by combining reaction and distillation in a single equipment. This unit operation is called "Reactive Distillation". Extensive literature is available providing the details of the development and application of the process.[1-6]. The development of the process has lead to

the requirement of the specific designing and modeling criteria.

The conceptual designing of any distillation column (Reactive or non-reactive) can have following tools

- VLE and Distillation Lines
- Flash Calculation
- Residue Curve Map (RCM)

To design the distillation column prior knowledge of Vapour-Liquid equilibrium is essential. However equilibrium in reactive distillation systems is more complex since the chemical equilibrium is super imposed on VLE. Different approaches followed are as shown in Table 1.

Table 1. Different Approach for finding out the VLE in Reactive Distillation

Sr. No.	Approach	Reference
1.	Combination of Chemical and Phase Equilibrium	1
2.	Element Balance	5,7
3.	Transformed Composition Variable	8-11

Distillation Lines are operating lines at total reflux, where as RCM is the locus of the residual liquid left in the pan during open evaporation. Barbosa & Doherty 1988a,b and Ung & Doherty,1995a,b have developed Residue Curve Maps for Reacting systems with single reaction system as well as multi-reaction systems. Studies on Kinetically Controlled Reactive Distillation have been reported [4,12-14]. In this case we relieve the assumption of the equilibrium condition. Venimadhavan et al. 1995 derived a class of models for the study of the effects of kinetics on the residue curve map.

Scope of the Present Work

The modeling of the Reactive distillation column requires two steps. The first is the Thermodynamic Modeling, which involves the calculation of Reactive VLE and second is Process Modeling, which involves Distillation lines, RCM and Reactive Flash. In the present work the aforesaid tools have been obtained for Butyl Acetate system using MATLAB as, the mathematical software. Present work includes,

- Computation of Reactive VLE and Distillation Lines for Butyl Acetate system
- Reactive Flash calculation for Butyl Acetate system
- Residue Curve Mapping for Kinetically controlled RD for Butyl Acetate system

Butyl acetate system was chosen, as there is a little data available for the same as far as reactive distillation is concerned. For that forward rate constant was determined experimentally using PTSA as a catalyst. The value for the same is also collected from the literature [15].

Model Developments and Algorithms

Reactive VLE data Generation

Using the model equations one can develop different algorithms [1,2]. The isobaric algorithm is useful for generating reactive phase diagrams and boiling point surface diagrams. One should note that the limiting point value of 0 and 1 could only be approached but not attained, as there is no reaction under such conditions.

Two important modifications to the early algorithm [1] have been done. Firstly, instead of using Newton's method for recalculating temperature thermodynamic approach recalculates the temperature from the vapour pressure of a key component. Second modification is instead of comparing the activity coefficient at the end it is refined before the first time calculation of the vapour phase mole fraction so as to keep the iterations for the vapour phase calculation at minimum.

Residue Curve Mapping (RCM)

Simple Distillation

Consider a simple reactive distillation process, in which a single chemical reaction is taking place in a liquid phase only and the vapour is continuously removed from the still. Two cases are possible for this as,

1. Equilibrium is instantaneously established for reacting liquid phase.
2. Liquid phase compositions are controlled by kinetics

Equilibrium RCM: Let the simple reactive distillation proceed at equilibrium. The equation for the Residue Curve Map can be obtained by simple material balance equation for the individual components and over all material balance. The equation we get will be,

$$\frac{dX_i}{d\tau} = X_i - Y_i, i = 1, 2, \dots, C - 1, i \neq \text{ref} \quad (1)$$

The choice of reference component follows certain rules. [1]

Kinetically Controlled RCM: Consider again simple reactive distillation process as before (the only change is the reaction is not at equilibrium). The liquid phase reaction has the following stoichiometry and reaction rate,

$$A + B \rightleftharpoons C + D$$

$$r_A = -r_D = -k_f \left(x_A \gamma_A x_B \gamma_B - \frac{x_C \gamma_C x_D \gamma_D}{K} \right) \quad (2)$$

where, K is the thermodynamic equilibrium constant and k_f is the forward reaction rate constant. The rate based on activity can give accurate description of rate and equilibrium data. After some mathematical manipulation we get,

$$M1 = Da \left(x_A \gamma_A x_B \gamma_B - \frac{x_C \gamma_C x_D \gamma_D}{K} \right) e^{-\xi} \frac{k_f}{k_{f,\min}} \frac{V_0}{V} \quad (3a)$$

$$\frac{dx_i}{d\xi} = x_i - y_i - M1, i = 1, 2, 3 \quad (3b)$$

Where $d\xi = (V/H)dt$, and $Da = (H_0 k_{f,\min})/V_0$ (Damkohler No.)

Physically the Damkohler number can be defined as the dimensionless ratio of a characteristic liquid residence time (H_0/V_0) to the characteristic reaction time ($1/k_{f,\min}$). The quantity $k_{f,\min}$ is the value of forward rate constant at the lowest temperature on the boiling surface. (the lowest boiling azeotrope or pure component in the system). This is the basic equation that must be solved to obtain the residue curve for simple distillation with reaction. Heating policy that will give V/V_0 equal to H/H_0 will result in,

$$M2 = Da \left(x_A \gamma_A x_B \gamma_B - \frac{x_C \gamma_C x_D \gamma_D}{K} \right) \frac{k_f}{k_{f,\min}} \quad (4a)$$

$$\frac{dx_i}{d\xi} = x_i - y_i - M2, i = 1, 2, 3 \quad (4b)$$

With heating policy that will maintain $V=V_0$ for all times the equations 3 will become,

$$M3 = Da \left(x_A \gamma_A x_B \gamma_B - \frac{x_C \gamma_C x_D \gamma_D}{K} \right) e^{-\xi} \frac{k_f}{k_{f,\min}} \quad (5a)$$

$$\frac{dx_i}{d\xi} = x_i - y_i - M3, i = 1, 2, 3 \quad (5b)$$

Both of these models represent the simple distillation process subject to particular heating policy. In first case (equation 4) the model is autonomous, where as in the second case (equation 5) the model is non-autonomous. In the present work we have obtained the RCM for low values of Da (Kinetically controlled) and for very high value of Da (Equilibrium RCM).

Kinetically controlled RCM

Kinetically controlled RCM can be obtained using the algorithm discussed next. Damkohler No. can be assumed before the calculation of RCM.

1. Set the pressure of the system.
2. Find the lowest boiling point of the system at the set pressure.
3. Calculate the $k_{f,\min}$ at the lowest temperature.
4. Set any arbitrary starting liquid phase compositions of the components in the still.
5. Perform the BUBL T calculation and find out the equilibrium vapor composition and temperature.
6. Using this temperature calculate the equilibrium constant and forward rate constant.

- Integrate equation 4 or 5, depending upon the model chosen as autonomous or non-autonomous

Using the new values of liquid phase compositions repeat the procedure from step-5 onwards.

Reactive Flash

Simple material balance of a reactive flash stage will provide the mathematical model for reactive flash calculation. Using the modified KZ algorithm [17] the flash calculations are performed. The criteria for the check of the convergence of the fraction vaporized is,

$$S = \sum_{i=1}^N \frac{(kvalue-1)z_i}{1 + \phi(kvalue-1)} = 0 \quad (6)$$

With

$$kvalue = \left(\frac{\gamma_i P_i^{sat}}{P \phi_i} \right) \quad (7a)$$

$$kvalue = \left(\frac{\gamma_i P_i^{sat}}{P Z_i} \right) \quad (7b)$$

Some mathematical manipulation to the material balance equation will lead to,

$$\sum_{i=1}^N v_{ij} (\ln F_i^{out}(\epsilon_1, \epsilon_2, \dots, \epsilon_M) - \ln(\sum F_i^{out}(\epsilon_1, \epsilon_2, \dots, \epsilon_M))) - \ln K_z = 0 \quad (8)$$

ϵ_j 's are unknowns and K_z 's are defined as,

$$K_z = K_j \prod_{i=1}^N \left(\frac{\gamma_i}{(kvalue-1)\phi+1} \right)^{-v_{ij}} \quad (9)$$

Computations and Results

Reactive VLE and Distillation Line

Reactive VLE data has been obtained for system Butyl Acetate with two different activity coefficient models viz. modified UNIFAC [18] and NRTL [19]. The maximum reactant concentration achieved is 40% of the reactant at equilibrium. It also says that there is not any Reactive Azeotrope at these conditions. The value of equilibrium constant is between 1-1.5. The value reported in literature is between 6-7 [15]. The difference may be due to the reason that the Gibb's free energy for Butyl Acetate was not available from the literature and so has been estimated using the method of Joback. [20] The value of activity coefficient of water in NRTL model is remarkably less, which is due to the change in concentration of water as well as due to the temperature at equilibrium. As water is in dilute concentration, even a minor change in the composition can cause the change in the value of activity coefficient.

This data is used to generate Distillation lines for Butyl Acetate system. Different initial conditions are the equilibrium values obtained from the reactive VLE data generated. The vapour phase composition in equilibrium with liquid phase composition is allowed to condense.

Resulting liquid phase composition will reach to the reaction equilibrium at the condensation temperature. This will again produce the equilibrium vapour phase composition, and thus one can proceed to obtain equilibrium distillation lines. These lines shows that different starting values will end up at different distillates depending upon the stating conditions but the bottoms compositions approached is richer and richer in Butyl Acetate as the composition of the reactant decrease at equilibrium. The distillation lines are shown in **Figure 1**.

Reactive Flash

In the calculation of reactive flash MODIFIED UNIFAC and NRTL models are used for the computation of activity coefficients and SRK and PR equations of state are used for the computations of fugacity coefficients. Dimerisation coefficient is also considered. The data for Ethyl acetate and Butyl Acetate systems have been generated. The data for ethyl acetate system have been compared with that available in the literature [21]. Thus, the validity of the programme has been checked. The effect of dimerisation, which was not considered in the literature, has resulted in a slight deviation in the values.

For Butyl Acetate system, isobaric (P=1 atm) simulation is performed for two-process design variable,

- Fixed Temperature of flash (385 K) and various feed ratio of Acetic Acid (AA) and Butanol in the range of 1.5 to 0.666.
- Fixed feed ratio (1.5) of Butanol to AA and various temperatures in the range of 375 to 385.

The results are shown in Figures 2 and 3. The calculation is based on the expression of K estimated from thermodynamic data. The data obtained are from standard literature. [20,22-24] The computed values show the effect of feed ratio on conversion and fraction vaporized. It

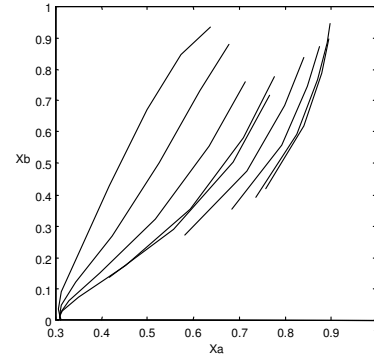


Figure 1. Distillation line for Butyl Acetate system

shows that the extent of reaction increase when one of the reactant is in excess and minimum at the stoichiometric feed as expected. The effect is more predominant when Butanol is used in excess. Fraction vaporized reduces with increase in AA. This might be due to the dimerisation of AA in the vapour phase. The concentration of the vapour phase Butyl Acetate will increase with increase in the Butanol to AA ratio.

The results for (b) are presented in **Figure 3**. As the temperature increases the extent of reaction increases and similarly the fraction vaporized increases. The latter is understandable and the former can be understood by the nature of the reaction, the reaction is endothermic in nature and so as the temperature increases the extent of reaction should increase. The concentration of Butyl Acetate will increase with increase in the temperature as the extent of reaction increases. One striking feature of the data for Butyl Acetate system is that the k value for AA is least among the all component. In fact the boiling point of AA is not the highest but the dimerisation may have affected the value.

Residue Curve Map

The simple reactive distillation behavior is simulated and concentration profile for Butyl Acetate and Acetic Acid were obtained using Da as a parameter (ranging from 0 to 50). The results were obtained for different situation but in the present work only those determined based on experiments are presented.

The RCM are generated in the form of nonlinear phase-plane trajectories on X_a versus X_b plots using dynamic response data produced by simulating the model equations for Kinetically controlled RCM. In this work both autonomous and non-autonomous model equations have been considered. The RCM generation is illustrated for two values of Da based on the analysis of simple reactive distillation studied.

1. $Da=0.5$ which indicates not slow but intermediate reaction velocities and hence give kinetically controlled RCM
2. $Da=50$ which indicates very fast reaction and the RCM generated are effectively treated as equilibrium RCM.

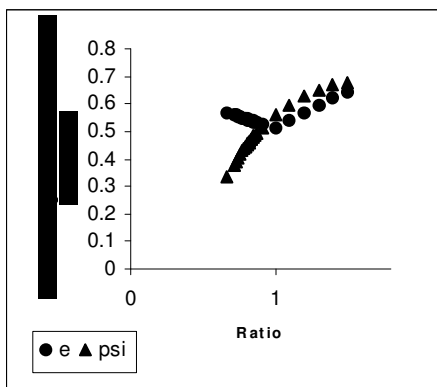


Figure 2 Effect of Reactant Ratio on Fraction Vaporised & Reaction coordinate

Kinetically Controlled RCM

The representative residue curve map is shown in **Figure 4**. One can observe that starting with different initial values the liquid phase composition approach the mixture of Butyl Acetate and Acetic Acid and all the curves if extended backwards approach water.

Equilibrium RCM

The RCM generated for equilibrium condition is as shown in **Figure 5**. The liquid phase composition, attained for different initial condition, is Butyl Acetate. The back calculation provides us with water or the heterogeneous azeotrope between Butanol and water.

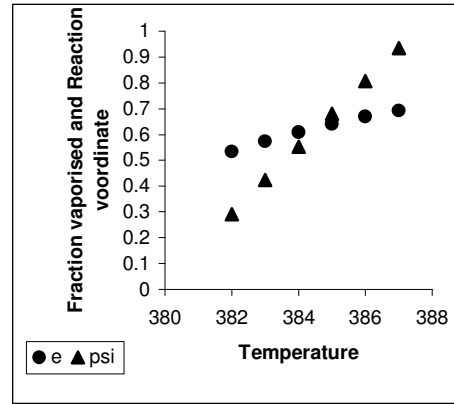


Figure 3. Effect of Temperature on Fraction Vaporised & Reaction Coordinate

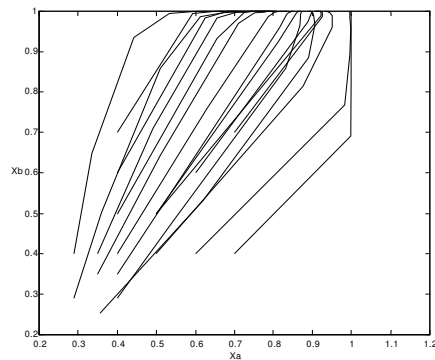


Figure 4. RCM for Non-Autonomous Model with $Da=0.5$

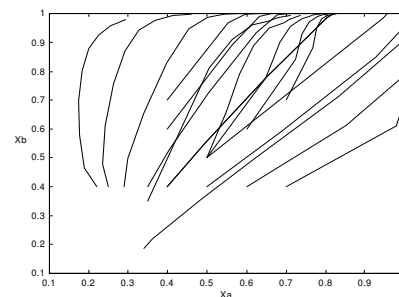


Figure 5. RCM for Autonomous Model with $Da=50$

Conclusion

Reactive VLE data suggest that the maximum reactant concentration achieved is 40% of the reactant at equilibrium. It also says that there is no Reactive Azeotrope at these conditions. Distillation line study says that it is

possible to obtain almost pure Butyl Acetate from the bottom without any distillation boundaries.

Reactive Flash calculations suggest that, the RD should be carried out using *excess of Butanol* and in the temperature range of 380-385 K. The Residue Curve Map studies imply that the stable node for kinetically controlled process is the mixture of Butyl Acetate and Acetic Acid, and for equilibrium process it is Butyl Acetate. The unstable node in both the case was found to be either pure water or the heterogeneous azeotrope between Butanol and Water. One can say from the same that reactive distillation process for Butyl Acetate can produced pure butyl acetate with some further designing and experimental consolidation.

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Nomenclature

Da	Damkohler number
Fin	initial moles of any component in the feed before the reaction has taken place
Fout	final moles of any component after the reaction has reached equilibrium
H	molal liquid hold up, moles
k_f	forward reaction rate constant, time ⁻¹
$k_{f,min}$	forward rate constant at the lowest temperature on the boiling surface, time ⁻¹
kvalue	phase equilibrium constant between liquid and vapour phase composition
K	reaction equilibrium constant
Ka	dimerisation constant, Pa ⁻¹
Kz	effective equilibrium constant defined for overall composition
M	No. of reaction
Psat	vapour pressure, Pa
X	transformed liquid phase composition
z,znew	over all composition
Z	compressibility factor

Greek letters

ϵ	extent of reaction
γ	activity coefficient
ϕ	fugacity coefficient
φ	fraction vapourised
τ	dimensionless time
ξ	wrap time